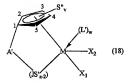
[00198] The preferred choice of transition metal component for the amorphous polymer fraction is the mono-cyclopentadienyl transition metal component of equation 10 where y is equal to 1. This preferred component is illustrated in equation 18:



where A', J, S', X1, X2, L', z and was are previously defined and M is titanium. Substituent S", is defined to be the same as S" in equation 10 where the subscript "v" denotes the carbon atom on the cyclopentadienyl ring to which the substituent is bonded and where there can be zero, two or four substituents, S", on the cyclopentadienyl ring provided that the cyclopentadienyl ring is symmetrically substituted. Symmetrically substituted is defined to mean that the cyclopentadienyl ring is substituted in the 2 and 5 positions and/or 3 and 4 positions with S" groups that are of approximately of the same steric bulk. Typically the size of these S" groups are within 2 carbons of each other. Thus a cyclopentadienyl substituted at the 2 and the 5 positions with methyl and ethyl respectively, or substituted at the 3 and the 4 positions with hexyl and octyl. respectively, would be considered symmetric. Likewise, the cyclopentadienyl ring may be substituted at all four sites with S" groups and be considered symmetric as long as each of the symmetrical pairs are of similar steric bulk. Additionally, two adjacent S"-groups in the 3 and 4 position may be linked to form a ring provided that the new ring is also symmetrically substituted.

[00199] Catalyst systems of this type are known to impart 2,1-mistakes when incorporating C3 and higher alpha-olefins. The pre-catalysts where S' is bonded to the nitrogen ligand (I) via a 3' carbon (for example when S' is tert-butyl or 1-adamantyl) have fewer 2,1-mistakes then when S' is bonded to the nitrogen ligand (I) via a 1' carbon (for example when S' is n-butyl, methyl, or benzyl) or 2' carbon (for example when S' is cyclododecyl, cyclohexyl, or sec-butyl). The 2,1-mistakes in the polymer backbone impart (CH₂)₂ units that can be beneficial to the polymer properties. Polymers of this type, the characterization of such polymers and the catalyst systems used to produce such polymers are described in US5,723,560 and is incorporated herein by reference. Lower Mw versions of such polymers can be produced by changing process condition, for example, by increasing reactor temperature.

1002001 Preferred mono-cyclopentadienyl transition metal compounds which, according to the present invention, provide catalyst systems which are specific to the production of atactic poly- alpha-olefins include: dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(1-adamantylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(t-butylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(s-butylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(n-butylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(exo-2norbornylamido) titanium dichloride. diethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido) titanium dichloride, diethylsilyl(tetramethylcyclopentadienyl)(exo-2-norbornylamido) titanium dichloride, diethylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido) titanium dichloride, diethylsilyl(tetramethylcyclopentadienyl)(1-adamantylamido) titanium dichloride, diethylsilyl(tetramethylcyclopentadienyl)(t-butylamido) titanium dichloride, methylene(tetramethylcyclopentadienyl)(cyclododecylamido)

titanium dichloride, methylene(tetramethyleyelopentadienyl)(exo-2norbornylamido) titanium dichloride,
methylene(tetramethyleyelopentadienyl)(eyelohexylamido) titanium dichloride,
methylene(tetramethyleyelopentadienyl)(1-adamantylamido) titanium dichloride,
methylene(tetramethyleyelopentadienyl)(t-butylamido) titanium dichloride,
ethylene(tetramethyleyelopentadienyl)(eyelododecylamido) titanium dichloride,
ethylene(tetramethyleyelopentadienyl)(exo-2-norbornylamido) titanium
dichloride, ethylene(tetramethyleyelopentadienyl)(eyelohexylamido) titanium
dichloride, ethylene(tetramethyleyelopentadienyl)(1-adamantylamido) titanium
dichloride, ethylene(tetramethyleyelopentadienyl)(1-butylamido) titanium
dichloride, dimethylsilyl(tetramethyleyelopentadienyl)(cyclohexylamido)
titanium dimethyl, dimethylsilyl(tetramethyleyelopentadienyl)(cyclohexylamido)
titanium dimethyl, dimethylsilyl(tetramethyleyelopentadienyl)(1-adamantylamido)
titanium dimethyl, dimethylsilyl(tetramethyleyelopentadienyl)(1-adamantylamido)
titanium dimethyl, dimethylsilyl(tetramethyleyelopentadienyl)(1-adamantylamido)

titanium dimethyl, dimethylsilyl(tetramethylcyclopentadienyl)(1-adamantylamido)
titanium dimethyl, dimethylsilyl(tetramethylcyclopentadienyl)(t-butylamido)
titanium dimethyl, dimethylsilyl(tetramethylcyclopentadienyl)(s-butylamido)
titanium dimethyl, dimethylsilyl(tetramethylcyclopentadienyl)(n-butylamido)
titanium dimethyl, dimethylsilyl(tetramethylcyclopentadienyl)(exo-2norbornylamido) titanium dimethyl,
diethylsilyl(tetramethylcyclopentadienyl)(cyclopentadienyl)(diethylsilyl(tetramethylcyclopentadienyl))
titanium dimethyl,

diethylsilyl(tetramethylcyclopentadienyl)(exo-2-norbornylamido) titanium dimethyl, diethylsilyl(tetramethylcyclopentadienyl)(exo-2-norbornylamido) titanium dimethyl, diethylsilyl(tetramethylcyclopentadienyl)(1-adamantylamido) titanium dimethyl, diethylsilyl(tetramethylcyclopentadienyl)(1-butylamido) titanium dimethyl, methylene(tetramethylcyclopentadienyl)(exo-2-norbornylamido) titanium dimethyl, methylene(tetramethylcyclopentadienyl)(exo-2-norbornylamido) titanium dimethyl, methylene(tetramethylcyclopentadienyl)(1-adamantylamido) titanium dimethyl, methylene(tetramethylcyclopentadienyl)(1-butylamido) titanium dimethyl, methylene(tetramethylcyclopentadienyl)(1-butylamido) titanium dimethyl, ethylene(tetramethylcyclopentadienyl)(1-butylamido) titanium dimethyl, ethylene(tetramethylcyclopentadienyl)(2-butylamido) titanium dimethyl, ethylene(tetramethylcyclopentadienyl)(2-butylamido) titanium dimethyl, ethylene(tetramethylcyclopentadienyl)(2-butylamido) titanium dimethyl, ethylene(tetramethylcyclopentadienyl)(2-butylamido)

titanium dimethyl, ethylene(tetramethylcyclopentadienyl)(cyclohexylamido) titanium dimethyl, ethylene(tetramethylcyclopentadienyl)(1-adamantylamido) titanium dimethyl, ethylene(tetramethylcyclopentadienyl)(t-butylamido) titanium dimethyl, dimethylsilyl(2,5-dimethylcyclopentadienyl)(cyclododecylamido) titanium dichloride, dimethylsilyl(2,5-dimethylcyclopentadienyl)(exo-2norbornylamido) titanium dichloride, dimethylsilyl(2,5dimethylcyclopentadienyl)(cyclohexylamido) titanium dichloride, dimethylsilyl(2,5-dimethylcyclopentadienyl)(1-adamantylamido) titanium dichloride, dimethylsilyl(2.5-dimethylcyclopentadienyl)(t-butylamido) titanium dichloride, dimethylsilyl(3,4-dimethylcyclopentadienyl)(cyclododecylamido) titanium dichloride, dimethylsilyl(3,4-dimethylcyclopentadienyl)(exo-2norbornylamido) titanium dichloride, dimethylsilyl(3.4dimethylcyclopentadienyl)(cyclohexylamido) titanium dichloride, dimethylsilyl(3.4-dimethylcyclopentadienyl)(1-adamantylamido) titanium dichloride, dimethylsilyl(3,4-dimethylcyclopentadienyl)(t-butylamido) titanium dichloride, dimethylsilyl(2-ethyl-5-methylcyclopentadienyl)(cyclododecylamido) titanium dichloride, dimethylsilyl(2-ethyl-5-methylcyclopentadienyl)(exo-2norbornylamido) titanium dichloride, dimethylsilyl(2-ethyl-5methylcyclopentadienyl)(cyclohexylamido) titanium dichloride, dimethylsilyl(2ethyl-5-methylcyclopentadienyl)(1-adamantylamido) titanium dichloride, dimethylsilyl(2-ethyl-5-methylcyclopentadienyl)(t-butylamido) titanium dichloride, dimethylsilyl(3-ethyl-4- methylcyclopentadienyl)(cyclododecylamido) titanium dichloride, dimethylsilyl(3-ethyl-4-methylcyclopentadienyl)(exo-2norbornylamido) titanium dichloride, dimethylsilyl(3-ethyl-4methylcyclopentadienyl)(cyclohexylamido) titanium dichloride, dimethylsilyl(3ethyl-4-methylcyclopentadienyl)(1-adamantylamido) titanium dichloride, dimethylsilyl(3-ethyl-4-methylcyclopentadienyl)(t-butylamido) titanium dichloride, dimethylsilyl(2-ethyl-3-hexyl-5-methyl-4octylcyclopentadienyl)(cyclododecylamido) titanium dichloride, dimethylsilyl(2ethyl-3-hexyl-5-methyl-4-octylcyclopentadienyl)(exo-2-norbornylamido) titanium dichloride, dimethylsilyl(2-ethyl-3-hexyl-5-methyl-4octylcyclopentadienyl)(cyclohexylamido) titanium dichloride, dimethylsilyl(2ethyl-3-hexyl-5-methyl-4-octylcyclopentadienyl)(1-adamantylamido) titanium dichloride, dimethylsilyl(2-ethyl-3-hexyl-5-methyl-4-octylcyclopentadienyl)(tbutylamido) titanium dichloride, dimethylsilyl(2tetrahydroindenyl)(cyclododecylamido) titanium dichloride, dimethylsilyl(2tetrahydroindenyl)(exo-2-norbornylamido) titanium dichloride, dimethylsilyl(2tetrahydroindenyl)(cyclohexylamido) titanium dichloride, dimethylsilyl(2tetrahydroindenyl)(1-adamantylamido) titanium dichloride, dimethylsilyl(2tetrahydroindenyl)(t-butylamido) titanium dichloride, dimethylsilyl(2.5dimethylcyclopentadienyl)(cyclododecylamido) titanium dimethyl. dimethylsilyl(2.5-dimethylcyclopentadienyl)(exo-2-norbornylamido) titanium dimethyl, dimethylsilyl(2,5-dimethylcyclopentadienyl)(cyclobexylamido) titanium dimethyl, dimethylsilyl(2,5-dimethylcyclopentadienyl)(1-adamantylamido) titanium dimethyl, dimethylsilyl(2.5-dimethylcyclopentadienyl)(t-butylamido) titanium dimethyl, dimethylsilyl(3,4dimethylcyclopentadienyl)(cyclododecylamido) titanium dimethyl, dimethylsilyl(3,4-dimethylcyclopentadienyl)(exo-2-norbornylamido) titanium dimethyl, dimethylsilyl(3,4-dimethylcyclopentadienyl)(cyclohexylamido) titanium dimethyl, dimethylsilyl(3,4-dimethylcyclopentadienyl)(1-adamantylamido) titanium dimethyl, dimethylsilyl(3,4-dimethylcyclopentadienyl)(t-butylamido) titanium dimethyl, dimethylsilyl(2-ethyl-5methylcyclopentadienyl)(cyclododecylamido) titanium dimethyl, dimethylsilyl(2ethyl-5-methylcyclopentadienyl)(exo-2-norbornylamido) titanium dimethyl, dimethylsilyl(2-ethyl-5-methylcyclopentadienyl)(cyclohexylamido) titanium dimethyl, dimethylsilyl(2-ethyl-5-methylcyclopentadienyl)(1-adamantylamido) titanium dimethyl, dimethylsilyl(2-ethyl-5-methylcyclopentadienyl)(t-butylamido) titanium dimethyl, dimethylsilyl(3-ethyl-4methylcyclopentadienyl)(cyclododecylamido) titanium dimethyl, dimethylsilyl(3-

ethyl-4-methylcyclopentadienyl)(exo-2-norbornylamido) titanium dimethyl.

dimethylsilyl(3-ethyl-4-methylcyclopentadienyl)(cyclohexylamido) titanium dimethyl, dimethylsilyl(3-ethyl-4-methylcyclopentadienyl)(1-adamantylamido) titanium dimethyl, dimethylsilyl(3-ethyl-4-methylcyclopentadienyl)(t-butylamido) titanium dimethyl, dimethylsilyl(2-ethyl-3-hexyl-5-methyl-4-octylcyclopentadienyl)(cyclododecylamido) titanium dimethyl, dimethylsilyl(2-ethyl-3-hexyl-5-methyl-4-octylcyclopentadienyl)(cyclohexylamido) titanium dimethyl, dimethylsilyl(2-ethyl-3-hexyl-5-methyl-4-octylcyclopentadienyl)(cyclohexylamido) titanium dimethyl, dimethylsilyl(2-ethyl-3-hexyl-5-methyl-4-octylcyclopentadienyl)(1-adamantylamido) titanium dimethyl, dimethylsilyl(2-ethyl-3-hexyl-5-methyl-4-octylcyclopentadienyl)(t-butylamido) titanium dimethyl, dimethylsilyl(2-ettrahydroindenyl)(cyclododecylamido) titanium dimethyl, dimethylsilyl(2-tetrahydroindenyl)(cyclohexylamido) titanium dimethyl, dimethylsilyl(2-tetrahydroindenyl)(cyclohexylamido) titanium dimethyl, dimethylsilyl(2-tetrahydroindenyl)(cyclohexylamido) titanium dimethyl, dimethylsilyl(2-tetrahydroindenyl)(1-adamantylamido) titanium dimethyl, dimethylsilyl(2-tetrahydroindenyl)(1-adamantylamido)

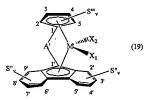
1002011 The most preferred species are:

titanium dimethyl.

tetrahydroindenyl)(t-butylamido) titanium dimethyl and the like.

dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(t-butylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(1-adamantylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(exo-2-norbornylamido) titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(tyclododecylamido) titanium dimethyl, dimethylsilyl(tetramethylcyclopentadienyl)(tyclohexylamido) titanium dimethyl, dimethylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido) titanium dimethyl, dimethylsilyl(tetramethylcyclopentadienyl)(1-adamantylamido) titanium dimethyl, adimethylsilyl(tetramethylcyclopentadienyl)(2-co-probornylamido)

[00202] Additionally, at higher reaction temperatures, some catalysts that produce syndiotactic poly- alpha-olefin at lower temperatures, will produce virtually non-crystalline poly- alpha-olefins at higher temperatures. The choice of transition metal component for this amorphous polymer fraction is a subset of the transition metal component of equations 8-9. Preferred components of this type are illustrated in equation 19:



wherein A', M, X_1 and X_2 are as previously defined. Substituents S^{**}_{v} and S^{***}_{v} are independently defined as S^{**} in equations 8-9 where the subscript "v" denotes the carbon atom on the Cp-ring or Flu-ring (fluorenyl-ring) to which the substituent is bonded.

[00203] Preferably metallocene precursors for producing poly-alpha-olefins having largely amorphous character (when used as catalysts under higher reactor temperature conditions) are those of Equation 19 where S'", are independently chosen such that the metallocene framework has a plane of symmetry containing the metal center and bisecting the Flu- and Cp-rings. The A' ligand need not be symmetrical – for example dimethylsilyl or methylphenylsilyl will not effect the stereochemisty of the polymer produced. Substituent S'", is defined to be the same as S" in equation 8-9 where the subscript "v" denotes the carbon atom on the cyclopentadienyl ring to which the substituent is bonded and where there can be zero, two or four substituents, S'", on the cyclopentadienyl ring provided that the

cyclopentadienyl ring is symmetrically substituted. Symmetrically substituted is defined to mean that the cyclopentadienyl ring is substituted in the 2 and 5 positions and/or 3 and 4 positions with S" groups that are of approximately of the same steric bulk. Typically the size of these S" groups are within 2 carbons of each other. Thus a cyclopentadienyl substituted at the 2 and the 5 positions with methyl and ethyl respectively, or substituted at the 3 and the 4 positions with hexyl and octyl, respectively, would be considered symmetric. Likewise, the cyclopentadienyl ring may be substituted at all four sites with S" groups and be considered symmetric as long as each of the symmetrical pairs are of similar steric bulk. Additionally, two adjacent S"-groups in the 3 and 4 position may be linked to form a ring provided that the new ring is also symmetrically substituted. Because of the distant placement of the S", substituents on the fluorenyl ring, these substitutents need not be symmetrically placed on the fluorenyl ring. Hence, the fluorenyl ring may be substituted with form 0-7 substituents that may be the same or different. Two or more adjacent S"-groups may optionally be linked to form a ring.

[00204] Preferred metallocene transition metal compounds which, according to the present invention, provide catalyst systems which are specific to the production of amorphous or low crystallinity poly- alpha-olefins include: isopropylidene(cyclopentadienyl)(fluorenyl) zirconium dichloride, isopropylidene(cyclopentadienyl)(fluorenyl) zirconium dichloride, methylene(cyclopentadienyl)(fluorenyl) zirconium dichloride, methylene(cyclopentadienyl)(fluorenyl) zirconium dichloride, diphenylmethylene(cyclopentadienyl)(fluorenyl) zirconium dimethyl, di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(fluorenyl) zirconium dimethyl, di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(fluorenyl) zirconium dichloride, di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(fluorenyl)

diphenylsilyl(cyclopentadienyl)(fluorenyl) zirconium dichloride. diphenylsilyl(cyclopentadienyl)(fluorenyl) zirconium dimethyl, dimethylsilyl(cyclopentadienyl)(fluorenyl) zirconium dichloride. dimethylsilyl(cyclopentadienyl)(fluorenyl) zirconium dimethyl, methylphenylsilyl(cyclopentadienyl)(fluorenyl) zirconium dichloride. methylphenylsilyl(cyclopentadienyl)(fluorenyl) zirconium dimethyl. isopropylidene(cyclopentadienyl)(fluorenyl) hafnium dichloride. isopropylidene(cyclopentadienyl)(fluorenyl) hafnium dimethyl. methylene(cyclopentadienyl)(fluorenyl) hafnium dichloride, methylene(cyclopentadienyl)(fluorenyl) hafnium dimethyl. diphenylmethylene(cyclopentadienyl)(fluorenyl) hafnium dichloride, diphenylmethylene(cyclopentadienyl)(fluorenyl) hafnium dimethyl, di(ptriethylsilylphenyl)methylene(cyclopentadienyl)(fluorenyl) hafnium dichloride. di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(fluorenyl) hafnium dimethyl, di(p-trimethylsilylphenyl)methylene(cyclopentadienyl)(fluorenyl) hafnium dichloride. di(p-trimethylsilylphenyl)methylene(cyclopentadienyl)(fluorenyl) hafnium dimethyl, diphenylsilyl(cyclopentadienyl)(fluorenyl) hafnium dichloride. diphenylsilyl(cyclopentadienyl)(fluorenyl) hafnium dimethyl, dimethylsilyl(cyclopentadienyl)(fluorenyl) hafnium dichloride, dimethylsilyl(cyclopentadienyl)(fluorenyl) hafnium dimethyl, methylphenylsilyl(cyclopentadienyl)(fluorenyl) hafnium dichloride, methylphenylsilyl(cyclopentadienyl)(fluorenyl) hafnium dimethyl,

isopropylidene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dichloride, isopropylidene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dichloride, methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, diphenylmethylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dichloride, diphenylmethylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl

 $\label{thm:continuity} idi(p-triethylsily|lphenyl)methylene(cyclopentadienyl)(3,8-di-t-buty|fluorenyl)\\ zirconium dichloride, di(p-triethylsily|lphenyl)methylene(cyclopentadienyl)(3,8-di-t-buty|fluorenyl) zirconium dimethyl, di(p-triethylsily|lphenyl)methylene(cyclopentadienyl)(3,8-di-t-buty|fluorenyl) zirconium dimethyl, di(p-triethylsily|lphenyl)methylene(cyclopentadienyl)(3,8-di-t-buty|fluorenyl) zirconium dimethyl, di(p-triethylsily|lphenyl)methylene(cyclopentadienyl)(3,8-di-t-buty|fluorenyl)$

trimethylsilylphenyl)methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl)
zirconium dichloride, di(p-trimethylsilylphenyl)methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, diphenylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, diphenylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, dimethylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, methylphenylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, methylphenylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, methylphenylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, methylphenylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) pafnium dimethyl, isopropylidene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dimethyl, methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dimethyl, diphenylmethylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dimethyl, diphenylmethylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dichloride, diphenylmethylene(cyclopentadienyl) (3,8-di-t-butylfluorenyl) hafnium dichloride, dichlorianyl) (3,8-di-t-butylfluorenyl) hafnium dichloride, dichlorianyl) (3,8-di-t-butylfluorenyl) hafnium dichloride, dichlorianyl) (3,8-di-t-butylfluorenyl) hafnium dichlori

triethylsilylphenyl)methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dichloride, di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dimethyl di(n-butylfluorenyl) hafnium dichloride hafnium dichl

trimethylsilylphenyl)methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl)
hafnium dichloride, di(p-trimethylsilylphenyl)methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dimethyl, diphenylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dichloride, diphenylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dimethyl, dimethylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dichloride, dimethylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dimethyl, methylphenylsilyl(cyclopentadienyl)(3,8-di-t-butylfluorenyl) hafnium dimethyl hafnium d

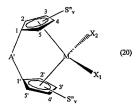
butylfluorenyl) hafnium dichloride, methylphenylsilyl(cyclopentadienyl)(3.8-di-tbutylfluorenyl) hafnium dimethyl, isopropylidene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) zirconium dichloride, isopropylidene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) zirconium dimethyl, methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) zirconium dichloride, methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) zirconium dimethyl, diphenylmethylene(cyclopentadienyl)(3.3.6.6.9.9.12.12-octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) zirconium dichloride. diphenylmethylene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) zirconium dimethyl, di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) zirconium dichloride, di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl] zirconium dimethyl. di(p-trimethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) zirconium dichloride. di(p-trimethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) zirconium dimethyl, diphenylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) zirconium dichloride, diphenylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzylfb.hlfluorenyl) zirconium dimethyl. dimethylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b.hlfluorenyl) zirconium dichloride. dimethylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) zirconium dimethyl,

methylphenylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) zirconium dichloride. methylphenylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzylfb.hlfluorenyl) zirconium dimethyl. isopropylidene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b.h]fluorenyl) hafnium dichloride. isopropylidene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) hafnium dimethyl. methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) hafnium dichloride, methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) hafnium dimethyl, diphenylmethylene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) hafnium dichloride, diphenylmethylene(cyclopentadienyl)(3.3.6.6.9.9.12.12-octamethyl-4.4.5.5.8.8.9.9-octahydrodibenzyl[b.h]fluorenyl) hafnium dimethyl. di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) hafnium dichloride, di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) hafnium dimethyl, di(p-trimethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12octamethyl-4.4.5.5.8.8.9.9-octahydrodibenzyl[b,h]fluorenyl) hafnium dichloride. di(p-trimethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12octamethyl-4.4.5.5.8.8.9.9-octahydrodibenzylfb.hlfluorenyl) hafnium dimethyl. diphenvlsilvl(cvclopentadienvl)(3.3.6.6.9.9.12.12-octamethvl-4.4.5.5.8.8.9.9octahydrodibenzyl[b,h]fluorenyl) hafnium dichloride. diphenylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) hafnium dimethyl, dimethylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9octahydrodibenzyl[b,h]fluorenyl) hafnium dichloride.

dimethylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) hafnium dimethyl,
methylphenylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) hafnium dichloride,
methylphenylsilyl(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) hafnium dimethyl, and the like.

[00205] The most preferred species are: di(ptriethylsilylphenyl)methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dichloride, di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(3,8-dit-butylfluorenyl) hafnium dichloride, di(ptriethylsilylphenyl)methylene(cyclopentadienyl)(3,8-di-t-butylfluorenyl) zirconium dimethyl, di(p-triethylsilylphenyl)methylene(cyclopentadienyl)(3,8-dit-butylfluorenyl) hafnium dimethyl, di(ptriethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9.12.12-octamethyl-4.4.5.5.8.8.9.9-octahydrodibenzyl[b,h]fluorenyl) zirconium dichloride, di(ptriethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4.4.5.5.8.8.9.9-octahydrodibenzyl[b,h]fluorenyl) hafnium dichloride, di(ptriethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4,4,5,5,8,8,9,9-octahydrodibenzyl[b,h]fluorenyl) zirconium dimethyl, and di(ptriethylsilylphenyl)methylene(cyclopentadienyl)(3,3,6,6,9,9,12,12-octamethyl-4.4.5.5.8.8.9.9-octahydrodibenzylfb.hlfluorenyl) hafnium dimethyl.

[00206] Additionally, compounds of formula 20 may be used to produce the amorphous polymer fraction.



[00207] In this case, S", are independently chosen such that the metallocene framework has a plane of symmetry that bisects M and A'. Substituents S", are independently defined to be the same as S" in equation 8-9 where the subscript "v" denotes the carbon atom on the cyclopentadienyl ring to which the substituent is bonded and where there can be zero to four substituents, S", on the cyclopentadienyl ring provided that the cyclopentadienyl ring is symmetrically substituted. Symmetrically substituted is defined to mean that the cyclopentadienyl ring is substituted in the 2 and 2'positions and/or 3 and 3' positions and/or 4 and 4' positions and/or 5 and 5' positions with S" groups that are of approximately of the same steric bulk. Typically the size of these S" groups are within 2 carbons of each other. Thus a cyclopentadienyl substituted at the 2 and the 2' positions with methyl and ethyl respectively, or substituted at the 3 and the 3' positions with hexyl and octyl, respectively, would be considered symmetric. Likewise, the cyclopentadienyl ring may be substituted at all four sites with S" groups and be considered symmetric as long as each of the symmetrical pairs are of similar steric bulk. Additionally, two adjacent S"-groups may be linked to form a ring provided that the new ring is also symmetrically substituted. Such complexes such as meso-Me,Si(indenyl),ZrMe, mesoCH₂CH₂(indenyl)₂ZrCl₂ are well known in the art and generally produce amorphous polymers useful in this invention.

[00208] Preferred meso-metallocene compounds which, according to the present invention, provide catalyst systems which are specific to the production of amorphous poly- alpha-olefins include the meso versions of: dimethylsilylbis(indenyl) zirconium dichloride, dimethylsilylbis(indenyl) zirconium dimethyl, diphenylsilylbis(indenyl) zirconium dichloride. diphenylsilylbis(indenyl) zirconium dimethyl, methylphenylsilylbis(indenyl) zirconium dichloride. methylphenylsilylbis(indenyl) zirconium dimethyl, ethylenebis(indenyl) zirconium dichloride, ethylenebis(indenyl) zirconium dimethyl, methylenebis(indenyl) zirconium dichloride, methylenebis(indenyl) zirconium dimethyl, dimethylsilylbis(indenyl) hafnium dichloride, dimethylsilylbis(indenyl) hafnium dimethyl, diphenylsilylbis(indenyl) hafnium dichloride. diphenylsilylbis(indenyl) hafnium dimethyl, methylphenylsilylbis(indenyl) hafnium dichloride, methylphenylsilylbis(indenyl) hafnium dimethyl, ethylenebis(indenyl) hafnium dichloride, ethylenebis(indenyl) hafnium dimethyl, methylenebis(indenyl) hafnium dichloride, methylenebis(indenyl) hafnium dimethyl, dimethylsilylbis(tetrahydroindenyl) zirconium dichloride. dimethylsilylbis(tetrahydroindenyl) zirconium dimethyl. diphenylsilylbis(tetrahydroindenyl) zirconium dichloride. diphenylsilylbis(tetrahydroindenyl) zirconium dimethyl. methylphenylsilylbis(tetrahydroindenyl) zirconium dichloride. methylphenylsilylbis(tetrahydroindenyl) zirconium dimethyl, ethylenebis(tetrahydroindenyl) zirconium dichloride, ethylenebis(tetrahydroindenyl) zirconium dimethyl, methylenebis(tetrahydroindenyl) zirconium dichloride. methylenebis(tetrahydroindenyl) zirconium dimethyl. dimethylsilylbis(tetrahydroindenyl) hafnium dichloride.

dimethylsilylbis(tetrahydroindenyl) hafnium dimethyl, diphenylsilylbis(tetrahydroindenyl) hafnium dichloride. diphenylsilylbis(tetrahydroindenyl) hafnium dimethyl, methylphenylsilylbis(tetrahydroindenyl) hafnium dichloride. methylphenylsilylbis(tetrahydroindenyl) hafnium dimethyl, ethylenebis(tetrahydroindenyl) hafnium dichloride, ethylenebis(tetrahydroindenyl) hafnium dimethyl, methylenebis(tetrahydroindenyl) hafnium dichloride, methylenebis(tetrahydroindenyl) hafnium dimethyl, dimethylsilylbis(2methylindenyl) zirconium dichloride, dimethylsilylbis(2-methylindenyl) zirconium dimethyl, diphenylsilylbis(2-methylindenyl) zirconium dichloride, diphenylsilylbis(2-methylindenyl) zirconium dimethyl, methylphenylsilylbis(2methylindenyl) zirconium dichloride, methylphenylsilylbis(2-methylindenyl) zirconium dimethyl, ethylenebis(2-methylindenyl) zirconium dichloride, ethylenebis(2-methylindenyl) zirconium dimethyl, methylenebis(2-methylindenyl) zirconium dichloride, methylenebis(2-methylindenyl) zirconium dimethyl. dimethylsilylbis(2-methylindenyl) hafnium dichloride, dimethylsilylbis(2methylindenyl) hafnium dimethyl, diphenylsilylbis(2-methylindenyl) hafnium dichloride, diphenylsilylbis(2-methylindenyl) hafnium dimethyl, methylphenylsilylbis(2-methylindenyl) hafnium dichloride. methylphenylsilylbis(2-methylindenyl) hafnium dimethyl, ethylenebis(2methylindenyl) hafnium dichloride, ethylenebis(2-methylindenyl) hafnium dimethyl, methylenebis(2-methylindenyl) hafnium dichloride, methylenebis(2methylindenyl) hafnium dimethyl, dimethylsilylbis(2-methyl-4-phenylindenyl) zirconium dichloride, diphenylsilylbis(2-methyl-4-phenylindenyl) zirconium dimethyl, diphenylsilylbis(2-methyl-4-phenylindenyl) zirconium dichloride. diphenylsilylbis(2-methyl-4-phenylindenyl) zirconium dimethyl, methylphenylsilylbis(2-methyl-4-phenylindenyl) zirconium dichloride, methylphenylsilylbis(2-methyl-4-phenylindenyl) zirconium dimethyl, ethylenebis(2-methyl-4-phenylindenyl) zirconium dichloride, ethylenebis(2methyl-4-phenylindenyl) zirconium dimethyl, methylenebis(2-methyl-4phenylindenyl) zirconium dichloride, methylenebis(2-methyl-4-phenylindenyl) zirconium dimethyl, dimethylsilylbis(2-methyl-4-phenylindenyl) hafnium dichloride, dimethylsilylbis(2-methyl-4-phenylindenyl) hafnium dimethyl, diphenylsilylbis(2-methyl-4-phenylindenyl) hafnium dichloride, diphenylsilylbis(2-methyl-4-phenylindenyl) hafnium dimethyl, methylphenylsilylbis(2-methyl-4-phenylindenyl) hafnium dichloride, methylphenylsilylbis(2-methyl-4-phenylindenyl) hafnium dimethyl, ethylenebis(2-methyl-4-phenylindenyl) hafnium dichloride, ethylenebis(2-methyl-4-phenylindenyl) hafnium dimethyl, methylenebis(2-methyl-4-phenylindenyl) hafnium dichloride, methylenebis(2-methyl-4-phenylindenyl) hafnium dimethyl. dimethylsilylbis(4.7-dimethylindenyl) zirconium dichloride, dimethylsilylbis(4.7dimethylindenyl) zirconium dimethyl, diphenylsilylbis(4,7-dimethylindenyl) zirconium dichloride, diphenylsilylbis(4,7-dimethylindenyl) zirconium dimethyl. methylphenylsilylbis(4,7-dimethylindenyl) zirconium dichloride, methylphenylsilylbis(4,7-dimethylindenyl) zirconium dimethyl, ethylenebis(4,7dimethylindenyl) zirconium dichloride, ethylenebis(4,7-dimethylindenyl) zirconium dimethyl, methylenebis(4,7-dimethylindenyl) zirconium dichloride. methylenebis(4,7-dimethylindenyl) zirconium dimethyl, dimethylsilylbis(4,7dimethylindenyl) hafnium dichloride, dimethylsilylbis(4.7-dimethylindenyl) hafnium dimethyl, diphenylsilylbis(4,7-dimethylindenyl) hafnium dichloride. diphenylsilylbis(4,7-dimethylindenyl) hafnium dimethyl, methylphenylsilylbis(4,7-dimethylindenyl) hafnium dichloride, methylphenylsilylbis(4,7-dimethylindenyl) hafnium dimethyl, ethylenebis(4,7dimethylindenyl) hafnium dichloride, ethylenebis(4,7-dimethylindenyl) hafnium dimethyl, methylenebis(4.7-dimethylindenyl) hafnium dichloride. methylenebis(4,7-dimethylindenyl) hafnium dimethyl, and the like.

[00209] The most preferred species are the racemic versions of: dimethylsilylbis(indenyl) zirconium dichloride, dimethylsilylbis(indenyl) zirconium dimethyl, ethylenebis(indenyl) zirconium dichloride, ethylenebis(indenyl) zirconium dimethyl, dimethylsilylbis(indenyl) hafnium dichloride, dimethylsilylbis(indenyl) hafnium dimethyl, ethylenebis(indenyl) hafnium dichloride, ethylenebis(indenyl) hafnium dimethyl, dimethylsilylbis(tetrahydroindenyl) zirconium dichloride. dimethylsilylbis(tetrahydroindenyl) zirconium dimethyl, ethylenebis(tetrahydroindenyl) zirconium dichloride. ethylenebis(tetrahydroindenyl) zirconium dimethyl, dimethylsilylbis(tetrahydroindenyl) hafnium dichloride, dimethylsilylbis(tetrahydroindenyl) hafnium dimethyl, ethylenebis(tetrahydroindenyl) hafnium dichloride, ethylenebis(tetrahydroindenyl) hafnium dimethyl, dimethylsilylbis(2-methylindenyl) zirconium dichloride, dimethylsilylbis(2-methylindenyl) zirconium dimethyl, ethylenebis(2methylindenyl) zirconium dichloride, ethylenebis(2-methylindenyl) zirconium dimethyl, dimethylsilylbis(2-methylindenyl) hafnium dichloride. dimethylsilylbis(2-methylindenyl) hafnium dimethyl, ethylenebis(2methylindenyl) hafnium dichloride, and ethylenebis(2-methylindenyl) hafnium dimethyl

[00210] When two transition metal compound based catalysts are used in one reactor as a mixed catalyst system, the two transition metal compounds should be chosen such that the two are compatible. A simple screening method such as by ¹H or ¹¹C NMR, known to those of ordinary skill in the art, can be used to determine which transition metal compounds are compatible.

[00211] It is preferable to use the same activator for the transition metal compounds, however, two different activators, such as a non-coordinating anion activator and an alumoxane, can be used in combination. If one or more transition metal compounds contain an X_1 or X_2 ligand which is not a hydride, hydrocarbyl, or substituted hydrocarbyl, then the alumoxane should be contacted with the

transition metal compounds prior to addition of the non-coordinating anion activator.

[00212] Particularly preferred combinations of transition metal compounds include:

- Me₂Si(Me₄C₂)(N-o-C₁₂H₂₀)TiCl₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrCl₂ (2-Me-4-PhInd = 2-methyl-4-phenylindenyl, c-C₁₂H₂₃ = cyclododecyl, Me₁C₂ tetramethylcyclopentadienyl) activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (2) Me₂Si(Me₄C₃)(N-c-C₁₁H₂)TiMe₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N₁N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (3) Me₂Si(Me₄C₂)(N-o-C₁₂H₂₀)TiCl₂ and rac-Me₂Si(2-MeInd)₂ZrCl₂ (2-MeInd = 2-methyl-indenyl) activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (4) Me₂Si(Me₄C₂)(N-c-C₁₁H₂₁)TiMe₂ and rac-Me₂Si(2-MeInd)₂ZtMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (5) Me,Si(Me,C₂)(N-1-adamantyl)TiCl₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;

- (6) Me₂Si(Me₄C₂)(N-1-adamantyl)TiMe₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylearbonium tetrakis(pentaflourophenyl)boron;
- (7) Me₂Si(Me₄C₃)(N-1-adamantyl)TiCl₂ and rac-Me₂Si(2-MeInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (8) Me₂Si(Me₄C₃)(N-1-adamantyl)TiMe₂ and rac-Me₂Si(2-MeInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- Me₂Si(Me₄C₂)(N-t-butyl)TiCl₂ and rac-Me₂Si(2-Me-4-Phind)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (10) Me₂Si(Me₄C₂)(N-t-butyl)TiMe₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylearbonium tetrakis(pentaflourophenyl)boron;
- (11) Me₂Si(Me₄C₂)(N-t-butyl)TiCl₂ and rac-Me₂Si(2-MeInd) activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (12) Me₂Si(Me₄C₂)(N-t-butyl)TiMe₂ and rac-Me₂Si(2-MeInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N.N-

- dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (13) Me₂Si(Me₂C₂)(N-exo-norbornyl)TiCl₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (14) Me₂Si(Me₄C₃)(N-exo-norbornyl)TiMe₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (15) Me,Si(Me,C₃)(N-exo-norbomyl)TiCl₂ and rac-Me,Si(2-MeInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (16) Me₂Si(Me₄C₂)(N-exo-norbornyl)TiMe₂ and rac-Me₂Si(2-MeInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N₂N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron:
- (17) (p-Et₃SiPh₂C(Cp)(3,8-di-t-BuFlu)HfCl₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrCl₂ (3,8-di-t-BuFlu = 3,8-di-tert-butylfluorenyl, Cp = cyclopentadienyl) activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (18) (p-Et₃SiPh)₂C(Cp)(3,8-di-t-BuFlu)HfMe₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N₂N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;

- (19) (p-Et₃SiPh)₂C(Cp)(3,8-di-t-BuFlu)HfCl₂ and rac-Me₂Si(2-MeInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (20) (p-Et₃SiPh)₂C(Cp)(3,8-di-t-BuFlu)HfMe₂ and rac-Me₂Si(2-MeInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron:
- (21) meso-CH₂CH₂(Ind)₂ZrCl₂ and rac-Me₂Si(H₄Ind)₂ZrCl₂ (Ind = indenyl, H₄Ind = tetrahydroindenyl) activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (22) meso-CH₂CH₂(Ind)₂ZrMe₂ and rac-Me₂Si(H₂Ind)₂ZrMe₂ activated with a non-coordinating anion activator, such as N₁N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (23) meso-CH₂CH₂(Ind)₂ZrCl₂ and rac-Me₃Si(2-MeInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (24) meso-CH₂CH₂(Ind)₂ZrMe₂ and rac-Me₂Si(2-MeInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N₂N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;

- (25) meso-Me₂Si(Ind)₂ZrCl₂ and rac-Me₂Si(H₄Ind)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane:
- (26) meso-Me,Si(Ind),ZrMe, and mc-Me,Si(H,Ind),ZrMe, activated with a non-coordinating anion activator, such as N,Ndimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (27) meso-Me₂Si(Ind),ZrCl₂ and rac-Me₂Si(2-MeInd),ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (28) meso-Me₂Si(Ind)₂ZrMe₂ and rac-Me₂Si(2-Melnd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N₂Ndimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (29) meso-Me,Si(2-MeInd),ZrCl₂ and rac-Me₂Si(2-Me-4-PhInd),ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (30) meso-Me₂Si(2-MeInd)₂ZrMe₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (31) meso-Me₂Si(2-MeInd)₂ZrCl₂ and rac-Me₂Si(2-MeInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;

- (32) meso-Me,Si(2-MeInd),ZrMe, and rac-Me,Si(2-MeInd),ZrMe, activated with a non-coordinating anion activator, such as N,Ndimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron:
- (33) meso-CH₂CH₂(2-MeInd)₂ZrCl₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (34) meso-CH₂CH₂(2-MeInd)₂ZrMe₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylearbonium tetrakis(pentaflourophenyl)boron;
- (35) meso-CH₂CH₂(2-MeInd)₂ZrCl₂ and rac-Me₂Si(2-MeInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (36) meso-CH₂CH₂(2-MeInd)₂ZrMe₂ and rac-Me₂Si(2-MeInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (37) meso-Me,Si(2-Me-4-PhInd),ZrCl₂ and rac-Me,Si(2-Me-4-PhInd),ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (38) meso-Me₂Si(2-Me-4-PhInd)₂ZrMe₂ and rac-Me₂Si(2-Me-4-PhInd)₂ZrMe₂ activated with a non-coordinating anion activator,

such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;

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- (39) meso-CH₂CH₂(2-Me-4-Phind),ZrCl₂ and rac-CH₂CH₂(2-Me-4-Phind),ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (40) meso-CH₂CH₂(2-Me-4-Phind)₂ZrMe₂ and rac-CH₂CH₃(2-Me-4-Phind)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylearbonium tetrakis(pentaflourophenyl)boron;
- (41) meso-CH₂CH₂(2-MeInd)₂ZrCl₂ and rac-CH₂CH₂(2-MePhInd)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane:
- (42) meso-CH₂CH₂(2-MeInd)₂ZrMe₂ and rac-CH₂CH₂(2-MeInd)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (43) meso-CH₂CH₂(Ind)₂ZrCl₂ and rac-CH₂CH₃(Ind)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (44) meso-CH₂CH₂(Ind)_ZrMe₂ and rac-CH₂CH₂(Ind)_ZrMe₂ activated with a non-coordinating anion activator, such as N₁Ndimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;

- (45) meso-Me₂Si(Ind)₂ZrCl₂ and rac-Me₂Si(Ind)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane:
- (46) meso-Me,Si(Ind),ZTMe, and rac-Me,Si(Ind),ZTMe, activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (47) meso-CH₂CH₂(Ind)₂ZrCl₂ and rac-CH₂CH₃(4,7-Me₂Ind)₂ZrCl₂ (4,7-Me₂Ind) = 4,7-dimethylindenyl) activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (48) meso-CH₂CH₂(Ind)₂ZrMe₂ and rac-CH₂CH₂(4,7-Me₂Ind)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylearbonium tetrakis(pentaflourophenyl)boron;
- (49) meso-Me₂Si(Ind)₂ZrCl₂ and rac-CH₂CH₂(4,7-Me₂Ind)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;
- (50) meso-Me₂Si(Ind)₂ZrMe₂ and rac-CH₂CH₂(4,7-Me₂Ind)₂ZrMe₂ activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron;
- (51) meso-CH₂CH₂(2-MeInd)₂ZrCl₂ and rac-CH₂CH₂(4,7-Me₂Ind)₂ZrCl₂ (4,7-Me₂Ind = 4,7-dimethylindenyl) activated with an alumoxane, such as methylalumoxane or modified methylalumoxane;

- (52) meso-CH₂CH₂(2-Melnd)₂ZrMe₂ and rac-CH₂CH₂(4,7-Me₂Ind)₂ZrMe₂ activated with a non-coordinating anion activator, such as N₂N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylearbonium tetrakis(pentaflourophenyl)boron;
- (53) meso-Me₂Si(2-Meind)₂ZrCl₂ and rac-CH₂CH₂(4,7-Me₂Ind)₂ZrCl₂ activated with an alumoxane, such as methylalumoxane or modified methylalumoxane; and
- (54) meso-Me, Joi(2-MeInd), ZrMe, and rac-CH, CH₂(4,7-Me, Ind), ZrMe, activated with a non-coordinating anion activator, such as N,N-dimethylanilinium tetrakis(pentaflourophenyl)boron or triphenylcarbonium tetrakis(pentaflourophenyl)boron.

[00213] The two transition metal compounds (pre-catalysts) may be used in any ratio. Preferred molar ratios of (A) transition metal compound to produce amorphous polymer to (B) transition metal compound to produce crystalline polymer fall within the range of (A:B) 1:1000 to 1000:1, alternatively 1:10 to 200:1, alternatively 1:10 to 500:1, alternatively 1:10 to 500:1, and alternatively 5:1 to 50:1. The particular ratio chosen will depend on the exact pre-catalysts chosen, the method of activation, and the end product desired. In a particular embodiment, when using the two pre-catalysts (A-"amorphous polymer producing precatalyst" and B-"crystalline polymer producing estalyst"), where both are activated with the same activator, the preferred mole percents, based upon the molecular weight of the pre-catalysts, are 10 to 99.9% A to 0.1 to 90%B, alternatively 25 to 99% A to 0.5 to 50% B, alternatively 50 to 99% A to 1 to 25% B, and alternatively 75 to 99% A to 1 to 10%B.

[00214] In general the combined pre-catalyst compounds and the activator are combined in ratios of about 1:10,000 to about 10:1. When alumoxane or aluminum alkyl activators are used, the combined pre-catalyst-to-activator molar ratio is from 1:5000 to 10:1, alternatively from 1:1000 to 10:1; alternatively, 1:500 to 2:1; or 1:300 to 1:1. When ionizing activators are used, the combined pre-catalyst-to-activator molar ratio is from 10:1 to 1:10; 5:1 to 1:5; 2:1 to 1:2; or 1:2:1 to 1:1. Multiple activators may be used, including using mixes of alumoxanes or aluminum alkyls with ionizing activators.

In another preferred embodiment a third catalyst (pre-catalyst plus [00215] activator) is present in the processes described above. The third catalyst may be any of the pre-catalyst components listed herein. Preferred third pre-catalysts include those that are capable of producing waxes. Preferred examples include: rac-dimethylsilylbis(4.7-dimethylindenyl) hafnium dichloride, racdimethylsilylbis(4.7-dimethylindenyl) hafnium dimethyl, rac-dimethylsilylbis(4.7dimethylindenyl) zirconium dichloride, rac-dimethylsilylbis(4,7-dimethylindenyl) zirconium dimethyl, rac-dimethylsilylbis(indenyl) hafnium dichloride. racdimethylsilylbis(indenyl) hafnium dimethyl, rac-dimethylsilylbis(indenyl) zirconium dichloride, rac-dimethylsilylbis(indenyl) zirconium dimethyl, racdimethylsilylbis(tetrahydroindenyl) hafnium dichloride, racdimethylsilylbis(tetrahydroindenyl) hafnium dimethyl, racdimethylsilylbis(tetrahydroindenyl) zirconium dichloride, racdimethylsilylbis(tetrahydroindenyl) zirconium dimethyl, rac-diphenylsilylbis(4,7dimethylindenyl) hafnium dichloride, rac-diphenylsilylbis(4,7-dimethylindenyl) hafnium dimethyl, rac-diphenylsilylbis(4,7-dimethylindenyl) zirconium dichloride, rac-diphenylsilylbis(4,7-dimethylindenyl) zirconium dimethyl, racdiphenylsilylbis(indenyl) hafnium dichloride, rac-diphenylsilylbis(indenyl) hafnium dimethyl, rac-diphenylsilylbis(indenyl) zirconium dichloride, rac-diphenylsilylbis(indenyl) zirconium dimethyl, rac-diphenylsilylbis(tetrahydroindenyl) hafnium dichloride,

rac-diphenylsilylbis(tetrahydroindenyl) hafnium dimethyl, racdiphenylsilylbis(tetrahydroindenyl) zirconium dichloride, racdiphenylsilylbis(tetrahydroindenyl) zirconium dimethyl, racmethylphenylsilylbis(4.7-dimethylindenyl) hafnium dichloride, racmethylphenylsilylbis(4,7-dimethylindenyl) hafnium dimethyl, racmethylphenylsilylbis(4.7-dimethylindenyl) zirconium dichloride, racmethylphenylsilylbis(4,7-dimethylindenyl) zirconium dimethyl, racmethylphenylsilylbis(indenyl) hafnium dichloride, racmethylphenylsilylbis(indenyl) hafnium dimethyl, racmethylphenylsilylbis(indenyl) zirconium dichloride, racmethylphenylsilylbis(indenyl) zirconium dimethyl, racmethylphenylsilylbis(tetrahydroindenyl) hafnium dichloride, racmethylphenylsilylbis(tetrahydroindenyl) hafnium dimethyl, racmethylphenylsilylbis(tetrahydroindenyl) zirconium dichloride, racmethylphenylsilylbis(tetrahydroindenyl) zirconium dimethyl, rac-ethylenebis(4,7dimethylindenyl) hafnium dichloride, rac-ethylenebis(4,7-dimethylindenyl) hafnium dimethyl, rac-ethylenebis(4,7-dimethylindenyl) zirconium dichloride. rac-ethylenebis(4.7-dimethylindenyl) zirconium dimethyl, racethylenebis(indenyl) hafnium dichloride, rac-ethylenebis(indenyl) hafnium dimethyl, rac-ethylenebis(indenyl) zirconium dichloride, rac-ethylenebis(indenyl) zirconium dimethyl, rac-ethylenebis(tetrahydroindenyl) hafnium dichloride, racethylenebis(tetrahydroindenyl) hafnium dimethyl, racethylenebis(tetrahydroindenyl) zirconium dichloride, and rac-ethylenebis(tetrahydroindenyl) zirconium dimethyl

[00216] Three transition metal compounds (pre-catalysts) may be used in any ratio. Preferred molar ratios of (A) transition metal compound to produce amorphous polypropylene to (B) transition metal compound to produce crystalline polypropylene to (C) transition metal compound to produce wax fall within the range of (A:B:C) 1:1000:500 to 1000:1:1, alternatively 1:100:50 to 500:1:1,

alternatively 1:10:10 to 200:1:1, alternatively 1:1:1 to 100:1:50, and alternatively 1:1:10 to 75:1:50, and alternatively 5:1:1 to 50:1:50. The particular ratio chosen will depend on the exact pre-catalysts chosen, the method of activation, and the end product desired.

[00217] Additional preferred catalysts and process are described in US Patents 6,376,410 and 6,380,122, which are incorporated by reference herein.

[00218] In another embodiment the catalyst compositions of this invention include a support material or carrier. For example, the one or more catalyst components and/or one or more activators may be deposited on, contacted with, vaporized with, bonded to, or incorporated within, adsorbed or absorbed in, or on, one or more supports or carriers.

[00219] The support material is any of the conventional support materials. Preferably the supported material is a porous support material, for example, tale, inorganic oxides and inorganic chlorides. Other support materials include resinous support materials such as polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl benzene polyolefins or polymeric compounds, zeolites, clays, or any other organic or inorganic support material and the like, or mixtures thereof.

[00220] The preferred support materials are inorganic oxides that include those Group 2, 3, 4, 5, 13 or 14 metal oxides. The preferred supports include silica, which may or may not be dehydrated, fumed silica, alumina (WO 99/60033), silica-alumina and mixtures thereof. Other useful supports include magnesia, titania, zirconia, magnesium chloride (U.S. Patent No. 5,965,477), montmortillonite (European Patent EP-B1 0 511 665), phyllosilicate, zeolites, talc, clays (U.S. Patent No. 6,034,187) and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina,

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silica-titania and the like. Additional support materials may include those porous acrylic polymers described in EP 0 767 184 B1, which is incorporated herein by reference. Other support materials include nanocomposites as described in PCT WO 99/47598, aerogels as described in WO 99/48605, spherulites as described in U.S. Patent No. 5,972,510 and polymeric beads as described in WO 99/50311, which are all herein incorporated by reference.

[00221] It is preferred that the support material, most preferably an inorganic oxide, has a surface area in the range of from about 10 to about 700 m²/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 5 to about 500 μ m. More preferably, the surface area of the support material is in the range of from about 50 to about 500 to about 500 m²/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 10 to about 200 μ m. Most preferably the surface area of the support material is in the range is from about 100 to about 400 m²/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 5 to about 100 μ m. The average pore size of the carrier useful in the invention typically has pore size in the range of from 10 to 1000Å, preferably 50 to about 500Å, and most preferably 75 to about 350Å.

[00222] As is well known in the art, the catalysts may also be supported together on one inert support, or the catalysts may be independently placed on two inert supports and subsequently mixed. Of the two methods, the former is preferred.

[00223] In another embodiment the support may comprise one or more types of support material which may be treated differently. For example one could use tow different silicas that had different pore volumes or had been calcined at different temperatures. Likewise one could use a silica that had been treated with a scavenger or other additive and a silica that had not.

[00224] The stereospecific catalysts may be used to prepare macromonomer having a Mw of 100,000 or less and a crystallinity of 30% or more preferably having vinyl termini.

[00225] As a specific example, a method for preparing propylene-based macromonomers having a high percentage of vinyl terminal bonds involves:

- a) contacting, in solution, propylene, optionally a minor amount of copolymerizable monomer, with a catalyst composition containing the stereorigid, activated transition metal catalyst compound at a temperature from about 80°C. to about 140°C.; and
- recovering isotactic or syndiotactic polypropylene chains having number average molecular weights of about 2,000 to about 30,000
 Daltons.

[00226] Preferably, the solution comprises a hydrocarbon solvent. More preferably, the hydrocarbon solvent is aliphatic or aromatic. Also, the propylene monomers are preferably contacted at a temperature from 90°C. to 120°C. More preferably, a temperature from 95°C to 115°C is used. Most preferably, the propylene monomers are contacted at a temperature from 100°C to 110°C. Reactor pressure generally can vary from atmospheric to 345 MPa, preferably to 182 MPa. The reactions can be run in batch or in continuous mode. Conditions for suitable slurry-type reactions will also be suitable and are similar to solution conditions, the polymerization typically being run in liquid propylene under pressures suitable to such.

[00227] The catalyst pair selection criteria were discussed earlier. One catalyst typically is stereospecific with the ability to produce significant population of vinyl-terminated macromonomers, the other typically is a specific

and capable of incorporating the reactive macromonomers. In general it is believed that C2 symmetric bulky ligand metallocene catalysts can produce vinyl terminated isotactic polypropylene macromonomers. Catalysts that favor betamethyl-elimination also often appear to also favor isotactic polypropylene macromonomer formation. Rac-dimethylsilyl bis(indenyl)hafnium dimethyl, dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dichloride, and rac-ethylene bis(4,7-dimethylindenyl) hafnium dimethyl are catalysts capable of producing isotactic polypropylene having high vinyl chain termination for use in this invention. High temperatures, typically above 80°C, appear to positively influence vinyl termination. Likewise, Me₂Si(Me₂C₂)(N-c-C₂H₂₂)TiMe₂ and Me₂Si(Me₄C₂)(N-c-C₂H₂₂)TiMe₂ produce amorphous polypropylene useful in this invention and are believed to incorporate the vinyl terminated macromonomers to also produce a grafted structure of sePP side chains on an amorphous backbone.

[00228] In alternate embodiments dienes such as 1,9-decadiene are introduced into the reaction zone to promote the production of vinyl-terminated aPP and scPP macromonomers that help increase the population of branch-block species.

Polymerization Processes

[00229] The catalysts and catalyst systems described above are suitable for use in a solution, bulk, gas or slurry polymerization process or a combination thereof, preferably solution phase or bulk phase polymerization process.

[60230] In one embodiment, this invention is directed toward the solution, bulk, slurry or gas phase polymerization reactions involving the polymerization of one or more of monomers having from 3 to 30 carbon atoms, preferably 3-12 carbon atoms, and more preferably 3 to 8 carbon atoms. Preferred monomers include one or more of propylene, butene-1, pentene-1, 4-methyl-pentene-1,

hexene-1, octone-1, decene-1, 3-methyl-pentene-1, and cyclic olefins or a combination thereof. Other monomers can include vinyl monomers, diolefins such as dienes, polyenes, norbomene, norbomadiene, vinyl norbomene, ethylidene norbomene monomers. Preferably a homopolymer or copolymer of propylene is produced. In another embodiment, both a homopolymer of propylene and a copolymer of propylene and one or more of the monomers listed above are produced.

F002311 One or more reactors in series or in parallel may be used in the present invention. Catalyst component and activator may be delivered as a solution or slurry, either separately to the reactor, activated in-line just prior to the reactor, or preactivated and pumped as an activated solution or slurry to the reactor. A preferred operation is two solutions activated in-line. For more information on methods to introduce multiple catalysts into reactors, please see US 6.399.722, and WO0130862A1. While these references may emphasize gas phase reactors, the techniques described are equally applicable to other types of reactors, including continuous stirred tank reactors, slurry loop reactors and the like. Polymerizations are carried out in either single reactor operation, in which monomer, comonomers, catalyst/activator, scavenger, and optional modifiers are added continuously to a single reactor or in series reactor operation, in which the above components are added to each of two or more reactors connected in series. The catalyst components can be added to the first reactor in the series. The catalyst component may also be added to both reactors, with one component being added to first reaction and another component to other reactors.

[00232] In one embodiment 500 ppm or less of hydrogen is added to the polymerization, or 400ppm or less, or 300 ppm or less. In other embodiments at least 50 ppm of hydrogen is added to the polymerization, or 100 ppm or more, or 150 ppm or more.

Gas phase polymerization

[00233] Generally, in a fluidized gas bed process used for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See for example U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228 all of which are fully incorporated herein by reference.)

Slurry phase polymerization

[00234] A slurry polymerization process generally operates between 1 to about 50 atmosphere pressure range (15 psi to 735 psi, 103 kPa to 5068 kPa) or even greater and temperatures in the range of 0°C to about 120°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which monomer and comonomers along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used the process must be operated above the reaction diluent critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

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[00235] In one embodiment, a preferred polymerization technique useful in the invention is referred to as a particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in for instance U.S. Patent No. 3,248,179 which is fully incorporated herein by reference. The preferred temperature in the particle form process is within the range of about 85°C to about 110°C. Two preferred polymerization methods for the slurry processes are those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Patent No. 4,613,484, which is herein fully incorporated by reference.

[00236] In another embodiment, the slurry process is carried out continuously in a loop reactor. The catalyst, as a slurry in isobutane or as a dry free flowing powder, is injected regularly to the reactor loop, which is itself filled with circulating slurry of growing polymer particles in a diluent of isobutane containing monomer and comonomer. Hydrogen, optionally, may be added as a molecular weight control. (In one embodiment 500 ppm or less of hydrogen is added, or 400 ppm or less or 300 ppm or less. In other embodiments at least 50 ppm of hydrogen is added, or 100 ppm or more, or 150 ppm or more.)

[00237] The reactor is maintained at a pressure of 3620 kPa to 4309 kPa and at a temperature in the range of about 60 °C to about 104 °C depending on the desired polymer melting characteristics. Reaction heat is removed through the loop wall since much of the reactor is in the form of a double-jacketed pipe. The slurry is allowed to exit the reactor at regular intervals or continuously to a heated low pressure flash vessel, rotary dryer and a nitrogen purge column in sequence for removal of the isobutane diluent and all unreacted monomer and comonomers.

The resulting hydrocarbon free powder is then compounded for use in various applications.

[00238] In another embodiment, the reactor used in the slurry process useful in the invention is capable of and the process useful in the invention is producing greater than 2000 lbs. of polymer per hour (907 Kg/hr), more preferably greater than 5000 lbs./hr (2268 Kg/hr), and most preferably greater than 10,000 lbs./hr (4540 Kg/hr). In another embodiment the slurry reactor used in the process useful in the invention is producing greater than 15,000 lbs. of polymer per hour (6804 Kg/hr), preferably greater than 25,000 lbs./hr (11,340 Kg/hr) to about 100,000 lbs./hr (45,500 Kg/hr).

[00239] In another embodiment in the slurry process useful in the invention the total reactor pressure is in the range of from 400 psig (2758 kPa) to 800 psig (5516 kPa), preferably 450 psig (3103 kPa) to about 700 psig (4827 kPa), more preferably 500 psig (3448 kPa) to about 650 psig (4828 kPa), most preferably from about 525 psig (3620 kPa) to 625 psig (4399 kPa).

[00240] In yet another embodiment in the slurry process useful in the invention the concentration of predominant monomer in the reactor liquid medium is in the range of from about 1 to 10 weight percent, preferably from about 2 to about 7 weight percent, more preferably from about 2.5 to about 6 weight percent, most preferably from about 3 to about 6 weight percent.

[00241] Another process useful in the invention is where the process, preferably a slurry process is operated in the absence of or essentially free of any scavengers, such as triethylaluminum, trimethylaluminum, tri-isobutylaluminum and tri-n-hexylaluminum and diethyl aluminum chloride, dibutyl zinc and the like. This process is described in PCT publication WO 96/08520 and U.S. Patent No. 5,712,352, which are herein fully incorporated by reference.

[00242] In another embodiment the process is run with scavengers. Typical scavengers include trimethyl aluminum, tri-isobutyl aluminum and an excess of alumovane or modified alumovane.

Homogeneous, bulk, or solution phase polymerization

[00243] The catalysts described herein can be used advantageously in homogeneous solution processes. Generally this involves polymerization in a continuous reactor in which the polymer formed and the starting monomer and catalyst materials supplied, are agitated to reduce or avoid concentration gradients. Suitable processes operate above the melting point of the polymers at high pressures, from 1 to 3000 bar (10-30,000 MPa), in which the monomer acts as diluent or in solution polymerization using a solvent.

[00244] Temperature control in the reactor is obtained by balancing the heat of polymerization with reactor cooling by reactor jackets or cooling coils to cool the contents of the reactor, auto refrigeration, pre-chilled feeds, vaporization of liquid medium (diluent, monomers or solvent) or combinations of all three.

Adiabatic reactors with pre-chilled feeds may also be used. The reactor temperature depends on the catalyst used. In general, the reactor temperature preferably can vary between about 30°C and about 160°C, more preferably from about 90°C to about 150°C, and most preferably from about 100°C to about 150°C, and most preferably from about 100°C to about 100°C to about 100°C. In series a dilimine Ni catalyst may be used at 40°C, while a metallocene Ti catalyst can be used at 100°C or more. In series operation, the second reactor temperature is preferably higher than the first reactor temperature. In parallel reactor operation, the temperatures of the two reactors are independent. The pressure can vary from about 1 mm He to 2500 bar (25.000 MPa), preferably from

0.1 bar to 1600 bar (1-16,000 MPa), most preferably from 1.0 to 500 bar (10-5000MPa).

[00245] In one embodiment 500 ppm or less of hydrogen is added to the polymerization, or 400 ppm or less or 300 ppm or less. In other embodiments at least 50 ppm of hydrogen is added to the polymerization, or 100 ppm or more, or 150 ppm or more.

[00246] Each of these processes may also be employed in single reactor, parallel or series reactor configuratious. The liquid processes comprise contacting olefin monomers with the above described catalyst system in a suitable diluent or solvent and allowing said monomers to react for a sufficient time to produce the desired polymers. Hydrocarbon solvents are suitable, both aliphatic and aromatic. Alkanes, such as hexane, pentane, isopentane, and octane, are preferred.

[40247] The process can be carried out in a continuous stirred tank reactor, batch reactor or plug flow reactor, or more than one reactor operated in series or parallel. These reactors may have or may not have internal cooling or heating and the monomer feed may or may not be refrigerated. See the general disclosure of U.S. patent 5,001,205 for general process conditions. See also, international application WO 96/33227 and WO 97/22639. All documents are incorporated by reference for US purposes for description of polymerization processes, metallocene selection and useful scavening compounds.

[00248] This invention further relates to a continuous process to prepare an adhesive comprising:

- combining monomer, optional solvent, catalyst and activator in a reactor system.
- withdrawing polymer solution from the reactor system,
- 3) removing at least 10% solvent, if present, from the polymer

solution,

- quenching the reaction,
- devolatilizing the polymer solution to form molten polymer,
- 6) combining the molten polymer and one or more additives (such as those described below) in a mixer, such as a static mixer, (in a preferred embodiment tackifier is not added or is added in amounts of less than 30 weight%, preferably less than 20 weight%, more preferably in amounts of less than 10 weight%),
 - 7) removing the polymer combination from the mixer, and
 - pelletizing or drumming the polymer combination;
 where step 1) comprises any of the processes described above.

[00249] In another embodiment this invention relates to a continuous process to prepare an adhesive comprising:

- combining monomer, optional solvent, catalyst and activator in a reactor system.
- withdrawing polymer solution from the reactor system,
- removing at least 10% solvent, if present, from the polymer solution.
- 4) quenching the reaction,
- devolatilizing the polymer solution to form molten polymer,
- combining the molten polymer and one or more additives in a mixer, such as a static mixer,
- removing the polymer combination from the mixer, and
- pelletizing or drumming the polymer combination.

[00250] In a particularly preferred embodiment, this invention relates to a continuous process to make an adhesive comprising

- selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less and a crystallinity of 20% or less under selected polymerization conditions;
- selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 40% or more at the selected polymerization conditions;
- 3) contacting, in a solvent and in a reaction zone under the selected polymerization conditions, the catalyst components in the presence of one or more activators with one or more C3 to C40 olefins, and, optionally one or more diolefins;
- 4) at a temperature of greater than 100°C;
- at a residence time of 120 minutes or less (preferably 60 to 120 minutes);
- 6) wherein the ratio of the first catalyst to the second catalyst is from 1:1 to 50:1:
- wherein the activity of the catalyst components is at least 50 kilograms of polymer per gram of the catalyst components; and wherein at least 20% of the olefins are converted to polymer;
- 8) withdrawing polymer solution from the reaction zone;
- removing at least 10% solvent from the polymer solution;
- 10) quenching the reaction;
- 11) devolatilizing the polymer solution to form molten polymer;
- combining the molten polymer and one or more additives in a mixer, such as a static mixer;
- 13) removing the polymer combination from the mixer; and
- 14) pelletizing or drumming the polymer combination.

[00251] In a particularly preferred embodiment, this invention relates to a continuous process to make an adhesive comprising

- selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less and a crystallinity of 20% or less under selected polymerization conditions;
- selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 40% or more at the selected polymerization conditions;
- contacting, in a solvent and in a reaction zone under the selected polymerization conditions, the catalyst components in the presence of one or more activators with one or more C3 to C40 olefins, and, optionally one or more diolefins;
- at a temperature of greater than 100°C;
- at a residence time of 120 minutes or less;
- 6) wherein the ratio of the first catalyst to the second catalyst is from 1:1 to 50:1;
- wherein the activity of the catalyst components is at least 50 kilograms of polymer per gram of the catalyst components; and wherein at least 50% of the olefins are converted to polymer;
- withdrawing polymer solution from the reaction zone;
- 9) removing at least 10% solvent from the polymer solution;
- quenching the reaction;
- 11) forming molten polymer
 - where the polymer comprises one or more C3 to C40 olefins, and less than 50 mole % of ethylene, and where the polymer has:
 - a) a Dot T-Peel of 1 Newton or more; and
 - a branching index (g') of 0.95 or less measured at the Mz of the polymer; and
 - an Mw of 100,000 or less; and
- combining the molten polymer and one or more additives in a mixer, such as a static mixer;
- 13) removing the polymer combination from the mixer; and

14) pelletizing or drumming the polymer combination.

[00252] In a particularly preferred embodiment, this invention relates to a continuous process to make an adhesive comprising

- selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less and a crystallinity of 20% or less under selected polymerization conditions;
- selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 40% or more at the selected polymerization conditions;
- contacting, in a solvent and in a reaction zone under the selected polymerization conditions, the catalyst components in the presence of one or more activators with one or more C3 to C40 olefins, and, optionally one or more diolefins;
- 4) at a temperature of greater than 100°C;
- 5) at a residence time of 120 minutes or less;
- 6) wherein the ratio of the first catalyst to the second catalyst is from 1:1 to 50:1:
- wherein the activity of the catalyst components is at least 50 kilograms of polymer per gram of the catalyst components; and wherein at least 50% of the olefins are converted to polymer;
- withdrawing polymer solution from the reaction zone;
- removing at least 10% solvent from the polymer solution;
- quenching the reaction;
- 11) forming molten polymer where the polymer comprises one or more C3 to C40 olefins (preferably propylene), and less than 50 mole % of ethylene, and where the polymer has:
 - a) a Dot T-Peel of 3 Newton or more; and
 - a branching index (g') of 0.90 or less measured at the Mz of

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the polymer; and

- an Mw of 30,000 or less;
- a peak melting point between 60 and 190°C,
- e) a Heat of fusion of 1 to 70 J/g,
- f) a melt viscosity of 8000 mPa•sec or less at 190°C; and
- 12) combining the molten polymer and one or more additives in a mixer, such as a static mixer;
- 13) removing the polymer combination from the mixer; and
- 14) pelletizing or drumming the polymer combination.

[00253] In another embodiment this invention relates to a continuous process to prepare an adhesive comprising:

- 1) combining monomer, catalyst and activator in a reactor system,
- withdrawing polymer from the reactor system,
- quenching the reaction, .
- forming molten polymer,
- 5) combining the molten polymer and one or more additives, and
- nelletizing or drumming the polymer combination.

Formulations of the polymers

[00254] The polymers produced herein then can be used directly as an adhesive or blended with other components to form an adhesive.

[00255] Tackifiers are typically not needed with the polymers of this invention. However if tackifier is desired, the tackifiers that may be blended with the polymers described above are those typically used in the art. Examples include, but are not limited to, aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadiene resins, gum rosins, gum rosin esters, wood rosins, wood

rosin esters, tall oil rosins, tall oil rosin esters, polyterpenes, aromatic modified polyterpenes, terpene phenolics. aromatic modified hydrogenated polycyclopentadiene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins, hydrogenated terpenes and modified terpenes, and hydrogenated rosin esters. In some embodiments the tackifier is hydrogenated. In other embodiments the tackifier is non-polar. (Non-polar meaning that the tackifier is substantially free of monomers having polar groups. Preferably the polar groups are not present, however if they are preferably they are not present at more that 5 weight %, preferably not more that 2 weight %, even more preferably no more than 0.5 weight %.) In some embodiments the tackifier has a softening point (Ring and Ball, as measured by ASTM E-28) of 80 °C to 150 °C, preferably 100 °C to 130 °C.

[00256] The tackifier, if present, is typically present at about 1 weight % to about 80 weight %, based upon the weight of the blend, more preferably 2 weight % to 40 weight %, even more preferably 3 weight % to 30 weight %.

[00257] Preferred hydrocarbon resins for use as tackifiers or modifiers include:

Resins such as C5/C6 terpene resins, styrene terpenes, alpha-methyl styrene terpene resins, C9 terpene resins, aromatic modified C5/C6, aromatic modified cyclic resins, aromatic modified dicyclopentadiene based resins or mixtures thereof Additional preferred resins include those described in WO 91/07472, US 5,571,867, US 5,171,793 and US 4,078,132. Typically these resins are obtained from the cationic polymerization of compositions containing one or more of the following monomers: C5 diolefins (such as 1-3 pentadiene, isoprene, etc); C5 olefins (such as 2- methylbutenes, cyclopentene, etc.); C6 olefins (such as hexcee), C9 vinylaromatics (such as styrene, alpha methyl styrene, vinyltoluene, indene, methyl indene, etc.); cyclics (such as

dicyclopentadiene, methyldicyclopentadiene, etc.); and or terpenes (such as limonene, carene, etc).

 Resins obtained by the thermal polymerization of dicyclopentadiene, and/or the thermal polymerization of dimers or oligomers of cyclopentadiene and /or methylcyclopentadiene, optionally with vinylaromatics (such as styrene, alpha-methyl styrene, vinyl toluene, indene, methyl indene).

[00258] The resins obtained after polymerization and separation of unreacted materials, can be hydrogenated if desired. Examples of preferred resins include those described in US 4,078,132; WO 91/07472; US 4,994,516; EP 0 046 344 A: EP 0 082 726 A: and US 5.171.793.

[00259] In another embodiment an adhesive composition comprising polymer product of this invention further comprises a crosslinking agent.
Preferred crosslinking agents include those having functional groups that can react with the acid or anhydride group. Preferred crosslinking agents include alcohols, multiols, amines, diamines and/or triamines. Examples of crosslinking agents useful in this invention include polyamines such as ethylenediamine, diethylenetriamine, hexamethylenediamine, diethylantinopropylamine, and/or menthanediamine.

[00260] In another embodiment an adhesive composition comprising the polymer product of this invention further comprises typical additives known in the art such as fillers, antioxidants, adjuvants, adhesion promoters, oils, and/or plasticizers. Preferred fillers include titanium dioxide, calcium carbonate, barium sulfate, silica, silicon dioxide, carbon black, sand, glass beads, mineral aggregates, tale, clay and the like. Preferred antioxidants include phenolic antioxidants, such as Irganox 1010, Irganox, 1076 both available from Ciba-Geigy. Preferred oils

include paraffinic or napthenic oils such as Primol 3 52, or Primol 876 available from ExxonMobil Chemical France, S.A. in Paris, France, Preferred plasticizers include polybutenes, such as Parapol 950 and Parapol 1300 available from ExxonMobil Chemical Company in Houston Texas. Other preferred additives include block, antiblock, pigments, processing aids, UV stabilizers, neutralizers, lubricants, surfactants and/or nucleating agents may also be present in one or more than one layer in the films. Preferred additives include silicon dioxide, titanium dioxide, polydimethylsiloxane, talc, dyes, wax, calcium sterate, carbon black, low molecular weight resins and glass beads. Preferred adhesion promoters include polar acids, polyaminoamides (such as Versamid 115, 125, 140, available from Henkel), urethanes (such as isocvanate/hydroxy terminated polyester systems, e.g. bonding agent TN/Mondur Cb-75(Miles, Inc.), coupling agents, (such as silane esters (Z-6020 from Dow Corning)), titanate esters (such as Kr-44 available from Kenrich), reactive acrylate monomers (such as sarbox SB-600 from Sartomer), metal acid salts (such as Saret 633 from Sartomer), polyphenylene oxide, oxidized polyolefins, acid modified polyolefins, and anhydride modified polyolefins.

[00261] In another embodiment the polymers of this invention are combined with less than 3 wt % anti-oxidant, less than 3 wt % flow improver, less than 10 wt % wax, and or less than 3 wt % crystallization aid.

[00262] Other optional components that may be combined with the polymer product of this invention are plasticizers or other additives such as oils, surfactants, fillers, color masterbatches, and the like. Preferred plasticizers include mineral oils, polybutenes, phthalates and the like. Particularly preferred plasticizers include phthalates such as diisoundecyl phthalate (DIUP), diisononylphthalate (DINP), dioctylphthalates (DOP) and the like. Particularly preferred oils include aliphatic naphthenic oils.

Other optional components that may be combined with the polymer [00263] product of this invention are low molecular weight products such as wax, oil or low Mn polymer, (low meaning below Mn of 5000, preferably below 4000, more preferably below 3000, even more preferably below 2500). Preferred waxes include polar or non-polar waxes, functionalized waxes, polypropylene waxes, polyethylene waxes, and wax modifiers. Preferred waxes include ESCOMER™ 101. Preferred functionalized waxes include those modified with an alcohol, an acid, a ketone, an anhydride and the like. Preferred examples include waxes modified by methyl ketone, maleic anhydride or maleic acid. Preferred oils include aliohatic napthenic oils, white oils or the like. Preferred low Mn polymers include polymers of lower alpha olefins such as propylene, butene, pentene, hexene and the like. A particularly preferred polymer includes polybutene having an Mn of less than 1000. An example of such a polymer is available under the trade name PARAPOLTM 950 from ExxonMobil Chemical Company. PARAPOLTM 950 is a liquid polybutene polymer having an Mn of 950 and a kinematic viscosity of 220cSt at 100 °C, as measured by ASTM D 445. In some embodiments the polar and non-polar waxes are used together in the same composition.

[00264] In some embodiments, however, wax may not be desired and is present at less than 5 weight %, preferably less than 3 weight %, more preferably less than 1 weight %, more preferably less than 0.5 weight %, based upon the weight of the composition.

[00265] In another embodiment the polymers of this invention have less than 30 weight% total of any combination of additives described above, preferably less than 25 weight%, preferably less than 20 weight %, preferably less than 15 weight %, preferably less than 10 weight%, preferably less than 5 weight%, based upon the weight of the polymer and the additives.